The Dissociation of Mercuric Oxide

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The Dissociation of Mercuric Oxide

A Study of Equilibrium in the System Mercury and Oxygen

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THE DISSOCIATION OF MERCURIC OXIDE

BY GUY B. TAYLOR

The extreme importance of mercury in scientific work and the ease with which it acquires a dirty appearance, sticking to glass, or forming very small globules which will not coalesce, make a study of the conditions under which this occurs of some interest. It has been assumed that these small globules are surrounded by a film of a foreign metallic oxide, but the same effect is observed when the non-oxidizable metals, silver, gold, or platinum, are the only other metals present.[1] The merest trace of any foreign metal will usually cause the mercury to leave a "tail" when run over an inclined surface.[2] We found that when oxygen is passed over pure mercury at 200° C, the surface remained bright, but the metal showed a decided tendency to adhere to porcelain and leave a "tail." The question now arises whether or not mercury itself is oxidized under ordinary atmospheric conditions and whether traces of other metals act as catalyzers for this reaction. A knowledge of equilibrium conditions in the system mercury, oxygen, and mercuric oxide is essential. An examination of the literature reveals little information regarding this subject, so the first object of this investigation has been the determination of the dissociation pressure of mercuric oxide at low temperatures.

Historical.—The relation between mercury and oxygen has played an important part in the development of chemistry. That a red substance was formed by heating mercury for a long time in the air was known to the Latin Geber of the thirteenth century. It was the decomposition of this red substance that led to the discovery of oxygen by Priestley, 1774. One of Lavoisier's earliest experiments in demonstrating the law of quantitative combination consisted in heating a closed system of mercury and air, noting the shrinkage of the air volume, and then recovering the same volume of gas by decomposing the red crystals formed.[3]

The first attempt at measuring the dissociation pressure of mercuric oxide was made by Myers,[4] who concluded that above 400° C the partial pressure of oxygen had no upper limit, but Myers' apparatus was defective as was pointed out at the time by Debray.[5]

Echols[6] undertook to determine the temperature at which oxygen and mercury combine by passing air or oxygen over the liquid metal. The oxide began to form at 450° C. The oxide when heated alone began to decompose at 630° C. His experiments are interesting merely as indicating points at which the rate of reaction becomes considerable. According to Pélabon[7] combination is complete at 180° C. Carnelley and Walker,[8] working with what they believed to be the hydroxide, state that dehydration is complete at 175° and that decomposition is rapid at 415° to 440°.

Pélabon's[9] work in determining equilibrium pressures in the system mercury and oxygen above 440° is the most important investigation of this subject. His method consisted in heating together mercury and oxygen in sealed tubes until equilibrium was established, then cooling suddenly and measuring the oxygen, from which its partial pressure at the temperature of the experiment was calculated. Two series of experiments were made, one with the mercury and oxygen in equivalent proportions and the other with mercury in excess. He found that in the second case (*i. e.*, with the partial pressure of the mercury equal to its saturation pressure) the partial pressure of the oxygen could be expressed by the formula:

$$\log p = -\frac{27569}{T} - 57.58 \log T + 203.94711$$

where p is pressure in mm of mercury at the absolute temperature T.

From this formula, M. J. Bertrand's equation for the pressure of saturated mercury vapor and considerations of the law of mass action, Pélabon was able to arrive at an expression for the relation between the absolute temperature

and partial pressure of oxygen when the two elements in equivalents are in equilibrium with the solid oxide,

$$\log p = -\frac{10529.8}{T} - 16.61 \log T + 64.58240.$$

His results are given as follows:

°C	*p* (observed) mm	*p* (calculated) mm
500	985	972
520	1392	1403
580	3610	3589
610	5162	5308

The temperatures were measured with a Le Chatelier thermo-element. No great accuracy was attempted.

Discussion.—The immediate object of our investigation has been to extend the dissociation pressure curve of mercuric oxide below 500° and downward as far as possible. Extrapolated values calculated from Pélabon's formula seem to indicate that the partial pressure of the oxygen falls off rapidly, thus at 450° C it is 337 mm, at 400° C 91.8, at 310° C 3.8 mm. Sufficiently accurate measures of volumes of oxygen as well as the difficulty of maintaining a constant temperature for a sufficient length of time at once exclude the sealed tube method for our purposes. For instance, Pélabon[10] found that at 440° C two days were required for equilibrium, while at 610° only one hour was necessary.

Of the two general methods available for measuring vapor or dissociation pressures, the static as ordinarily employed for oxides,[11] besides being open to all the objections of any static method,[12] is out of the question here since one of the dissociation products is easily condensible on the cold parts of the apparatus.[13] In the dynamic method, the principal difficulty encountered has been the slowness of the rate of reaction. For instance, in the apparatus to be described, a slow current of nitrogen was passed over the purest oxide (25 grams) heated to 468°. In 12 hours, 0.11 gram HgO

had been decomposed corresponding to a partial pressure of oxygen in the volume of nitrogen used of only 0.8 mm, while the true equilibrium partial pressure at this temperature proved to be five hundred times as great.

The vapor-pressure methods of Smith and Menzies[14] seem available for this study, provided the reaction can be made to occur with sufficient rapidity, *i. e.*, by catalysis. This we have been able to accomplish by certain metallic oxides.

The catalyses of solids, or reactions occurring in heterogeneous systems, do not seem to have been much investigated, except in the case of gases by contact substances, such as the formation of water from hydrogen and oxygen in the presence of silver,[15] or platinum,[16] on the well-known accelerating action of platinum or ferric oxide on the reaction $2SO_2 + O_2 = 2SO_3$. Few instances of catalysis of solids by solids are known. Many metallic oxides facilitate the escape of oxygen from potassium chlorate, but the reactions involved are complex.[17] A case more in point is the accelerating action of metallic silver on the decomposition of silver oxide, studied by Lewis.[18]

We have found that the decomposition of mercuric oxide is accelerated by finely divided platinum, ferric oxide, manganese dioxide, and cadmium oxide. Oxides like alumina and stannic oxide have no effect. There is no reason to suppose that there is any interaction in the case of the oxides. Each is at its highest state of oxidation and their dissociation pressures are altogether negligible at temperatures we have employed. As will be shown later in the dynamic method, mercury and oxygen are evolved in equivalents from mixtures of mercuric and ferric oxides.

Preparation of Pure Mercuric Oxide.—We have given considerable time and attention to a method for the preparation of pure oxide. That made from ignition of the nitrate almost certainly occludes oxides of nitrogen. The problem is to get mercury and oxygen to unite directly and rapidly. In experiments with this end in view, mixtures of mercury vapor and oxygen were passed over a glowing platinum wire

with no results. We also tried the effect of strong light by putting a Nernst glower directly in the neck of a flask containing mercury to which was fed oxygen under pressure. The rate of formation was not noticeably increased. When a large excess of mercury is heated with oxygen under pressure, a white scum first appears on the surface of the metal and then long needle crystals of the oxide.

As a final resort pure oxide was made by heating a large excess of mercury with oxygen in sealed tubes for several hours at 460°. The oxygen was prepared by electrolysis of sodium hydroxide solution in an especially constructed generator, and was passed over a glowing platinum wire, to free it from traces of hydrogen, and dried over calcium chloride. The air was carefully pumped out of each tube before filling with oxygen. All connections were glass. The mercury was distilled three times by the method of Hulett.[19] The excess of mercury was removed from the oxide by distillation in a current of oxygen. The process is a slow one and the yield not good. Much of the oxide adheres tightly to the glass and must be scraped off. The crystals obtained were large and transmitted yellow light. The material so prepared was our *normal oxide*.

Experimental

Temperature was measured with a platinum-platinum 10 percent rhodium thermoelement, and the electromotive force with a Wolff potentiometer against a standard saturated cadmium cell (1.01840 volts), maintained constantly at 25° in a thermostat.[20] This thermoelement was standardized at three different times during the course of this investigation and found not to have sensibly changed. Three fixed points were observed, the boiling points of water 100°, naphthalene 218°, and sulphur 444.5°. It was found that the readings in microvolts agreed exactly with the standard of Day and Sosman[21] at the water and naphthalene points, and read 20 microvolts lower at the boiling point of sulphur. A straight line deviation from Day and Sosman's curve[22] was plotted

and microvolts corresponding to every 10° from 300° to 480° were calculated. From the table so constructed the temperatures were read by interpolation and are therefore on the nitrogen gas scale.

Submerged Bulb Method.—A modification of this method as devised by Smith and Menzies[23] was employed. The bulb shown in Fig. 1 and made of thin lead-glass* tubing, was drawn out at one end into a capillary 0.5 to 1.0 mm in diameter. This capillary was bent around the bulb for the sake of compactness and not as shown in the figure, in one plane. At A was placed a small plug of glass wool and the bulb was filled as completely as possible from the lower end and sealed off at B. These bulbs were about 5 cm long and 1 cm diameter, and when filled contained about 5 grams of the oxide and an equal volume of catalyzer. The bulbs were designed to contain as large a quantity of oxide as was compatible with a small volume, so that a rapid stream of bubbles might be evolved.

Fig. 1

The essential features of the rest of the apparatus are shown in Fig. 2, a tall one-liter beaker containing melted sodium and potassium nitrate mixture and standing on a sand bath heated from below by a gas burner. An inverted beaker with its bottom cut out and resting on an inverted asbestos air bath supported on the legs of the tripod, served as a jacket. Efficient stirring of the 800 cc or more liquid was accomplished by means of a simple four-bladed propeller wheel carried on the end of a rapidly revolving stiff brass rod. The bulb (not shown in figure) was submerged completely under fused nitrates in the bottom of the long tube. This tube made of Jena glass was closed at the top by a rubber stopper, wired in, through which passed the quartz tube

* Lead glass does not crack when dropped suddenly into fused nitrates at 500° C.

carrying the thermoelement wires. The side tube provided connection to the pressure tank, suction pump, and manometer. The pressures were read on a simple open arm manometer in conjunction with a barometer. Readings were made to the nearest millimeter and corrections were made for submerged depth. Corrections for capillarity were not applied as they are well within the error of the measurement.

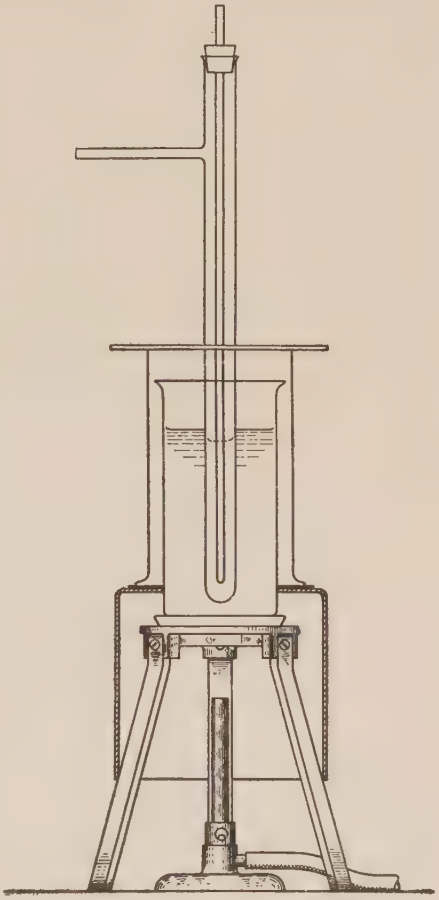

Fig. 2

First the bulb was thoroughly boiled out to expel all air and foreign gases by raising the temperature considerably above the boiling point of the solid HgO. The bubbling was none too fast so an hour was usually allowed. Then by carefully increasing the pressure a point was reached where bubbling almost ceased. The pressure was now fixed and the temperature very slowly lowered until the liquid began to rise in the capillary, when the temperature was taken to correspond to this fixed pressure. The pressure was then diminished and fixed, and the temperature allowed to fall until another point was located. The bubbling slowed up near the end points so much that we were obliged to exercise great caution lest the point be reached too soon, indicating temperatures higher than the

TABLE I—SUBMERGED BULB METHOD

	°C	Total pressure mm	Partial pressure (observed) mm	Oxygen (calc.) mm
Normal red oxide with Fe_2O_3	475.7	1430	476.7	482
	470.4	1290	430.0	430
	461.3	1058	352.7	351
	455.0	921	307.0	303
	452.5	856	285.3	285
	437.0	586	(195.3)	200
	411.7	308	(102.7)	107
	380.9	109	(36.3)	47
	356.4	39	(13.0)	28
Kahlbaum red oxide with Fe_2O_3	474.1	1394	464.7	465
	463.8	1096	365.3	369
	458.1	976	325.3	325
	450.9	830	276.7	276
	444.0	701	233.7	235
	425.4	449	149.7	148
Merck's red oxide with Fe_2O_3	476.2	1467	489.0	487
	471.3	1303	434.3	436
	465.8	1157	386.3	387
	458.2	982	327.3	326
	417.5	345	(115.0)	122
	404.2	236	(78.7)	87
	396.8	187	(62.3)	72
	363.8	67	(22.3)	32
Merck's red oxide with MnO_2	476.2	1451	483.7	487
	466.7	1175	391.7	392
	458.3	966	322.0	325
	453.0	863	287.7	287
	431.3	512	170.7	173
	420.8	395	131.7	133
Merck's red oxide with CdO	468.0	1217	405.7	406
	459.3	986	328.7	330
	447.8	773	257.7	257
	434.7	553	184.3	186
	421.5	403	134.3	136
	390.0	176	58.7	60

true ones and correspondingly low pressures. The reaction at the lower temperatures is so slow that the pressures indicated by this method are almost certainly too small.

Five series of observations were made as given above. About 5 grams of mercuric oxide were ground and passed through fine bolting cloth, and then mixed with about an equal volume of catalyst, similarly ground and bolted. The ferric oxide used was Kahlbaum's "Brown Label" marked "special," which was ignited before use. The cadmium and manganese oxides were also Kahlbaum's preparations, ordinary grade. Following the usage of Pélabon the results have been calculated to partial pressure of oxygen by dividing the observed pressures by three. Under the column headed "calculated" are given the values taken from our final curve.

Static Method.[25]—Here we used the isoteniscope modified by the insertion of a trap to catch the condensed mercury as shown in Fig. 3. The method permits fixing the temperature and adjusting the pressure, an advantage over the submerged bulb method. With fused nitrates as the confining liquid there was no interaction with the mercury vapor.

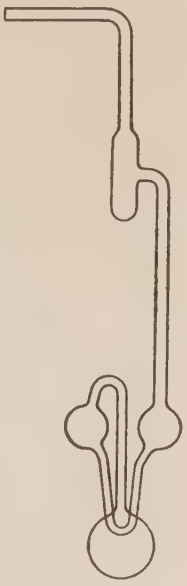

Fig. 3

The apparatus was charged with 5 grams oxide and the catalyst, immersed in the nitrate bath, and thoroughly boiled out. Then with temperature fixed, the pressure was carefully adjusted until the level of the liquid in the two arms remained stationary for some time, care of course being taken not to allow air to re-enter the bulb. The pressure was then reduced, the apparatus allowed to boil out for 15 to 20 minutes and the observation repeated. The response to a change in either pressure or temperature was very slow. The results are given in Table II.

TABLE II—STATIC METHOD

	° C	Total pressure	Partial pressure (observed) mm	Oxygen (calc.) mm
Red oxide with Fe_2O_3	480.0	1580	526.7	527
	469.0	1255	418.3	416
	463.8	1107	369.0	369
	451.7	845	281.7	281
	440.2	642	214.0	214
	436.2	591	197.0	195
	418.2	371	123.7	123
	403.3	252	84.0	84
	388.5	174	58.0	58
Red oxide with CdO	436.6	588	196.0	197
	403.8	260	86.7	86
	369.5	104	34.7	35

An attempt was made to measure the pressure at 480° by this method without a catalyst. In order to ensure the expulsion of all the air the apparatus was kept at 500° under 30 mm pressure for several hours, the temperature then lowered to 480° and the pressure increased as rapidly as the rate of decomposition would permit. At the end of 8 hours a pressure of 1507 mm was reached which was still increasing at the rate of 2 or 3 mm per hour. We then lowered the temperature 4°, and after the first fall of pressure due to contraction of the gases, there began a decrease at about the same rate. At 1486 mm the experiment was discontinued. It is clear that accurate measures could not have been obtained under these conditions, but the results are in harmony with those obtained with the aid of catalysts, and give confidence in them.

The Dynamic Method.—Beginning with Regnault[26] this method has been extensively used for vapor pressures particularly at lower temperatures.[27] Briefly it consists in saturating a known volume of an inert gas with the vapor of the substance, and from a knowledge of the quantity of the vapor calculating its partial pressure according to Dalton's law.

The apparatus for this method was practically perfected before we tried either of the other methods, for it was hoped that we would be able to determine directly the dissociation pressure of mercuric oxide at comparatively low temperatures, but the slow rate of decomposition has made this impossible even with a catalyst. We have only been able to confirm our results as obtained above.

The apparatus in its final form is shown in Fig. 4 and consists essentially of a reaction chamber, R, a purifying train for nitrogen gas (D, E, G), devices for collecting the mercury and oxygen, and the aspirator O. The most troublesome and, at the same time, important part of the apparatus is the heating arrangement for the reaction chamber, which must be fairly large in order to ensure saturation at equilibrium conditions. This large chamber must be uniformly heated and maintained at constant temperature for a considerable length of time. Electric heating of a cylindrical chamber seemed to fulfil these conditions best, so we set out to construct an electric resistance furnace that would heat a tube 25 cm long and 2.5 cm diameter uniformly its entire length, and we succeeded finally in getting one that dropped off less than 1° from its center to points 12 cm distant on either side at a temperature of 450° C.

A detailed section through the furnace is shown in Fig. 5. Nichrome wire, 2 mm diameter, was wound on a smooth wooden cylinder, 40 mm diameter, for a length of 56 cm. Exact uniformity in spacing was secured by winding on a lathe, the space between the wires being about the same as the diameter of the wire. Over the windings was wrapped tightly a layer of wet asbestos paper (0.75 mm thick), which was pressed down between the turns by winding No. 20 nickel wire in the spaces. Over this surface was spread a thin paste of magnesium oxide-water glass, filling all depressions and making a smooth cylinder, which when wrapped tightly in a thin sheet of asbestos fitted closely into a brass tube. This tube had the same length as the wire winding and a diameter only 6 mm more than the wooden core, hence the electrical

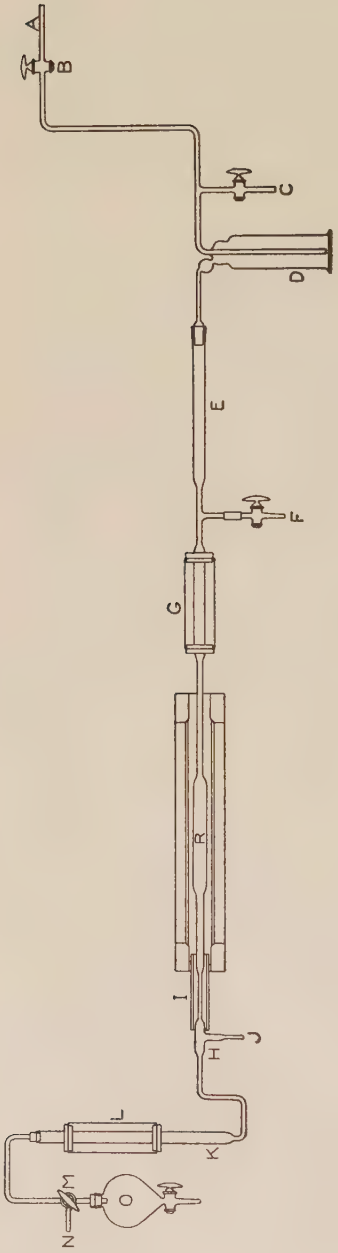

Fig. 4

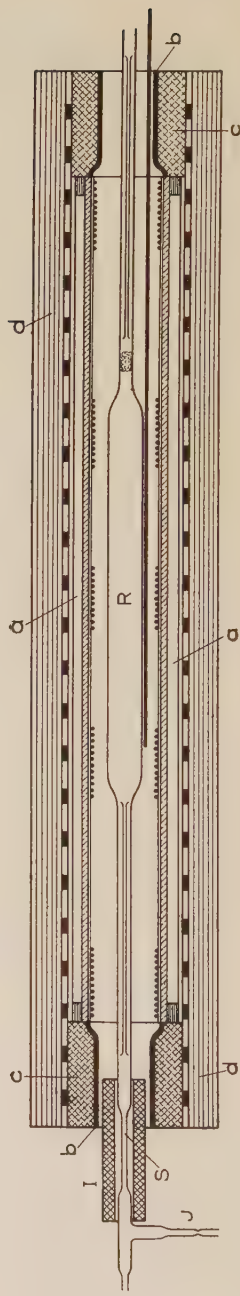

Fig. 5

insulation between brass and wire was 1 mm, making for equalization of temperature by the heat conductivity of the metal. The nichrome wires leading from the heater were wrapped with fine nickel wire to make them better conductors and were fastened securely by notches in the brass tube, being carefully insulated therefrom with mica. The nickel wire had no electrical connection. The wooden arbor was burnt out by boring a small hole longitudinally through it and then while in a perpendicular position, directing a pointed blast flame into the hole together with a current of air. The insulation was next thoroughly dried out by passing a current through a fine nichrome wire stretched through the middle of the tube. We now had a brass cylinder with a heating coil on the inside. The remaining details may be seen by reference to Fig. 5; *aa* is an air space whose outer wall is a glass cylinder. Covering this cylinder is a layer of heavy asbestos paper over which is wound an auxiliary heating coil of nichrome ribbon, serving to warm up the outer insulation and cutting down materially the time necessary to bring the furnace up to temperature; *bb* are porcelain cylinders packed in the ends with pulped asbestos, *cc*; the outer insulation *dd* is a wrapping of thin asbestos board.

The glass parts of the apparatus from E to L, Fig. 4, were made entirely of combustion tubing put together with an oxygen-gas blow pipe to avoid devitrification. The oxide and catalyst were charged in the chamber R. The entrance and exit for gases to this chamber were capillary size as shown in Fig. 5, in order that these gases might have as great velocity as possible. As capillary combustion tubing was not available, we resorted to the expedient of inserting ordinary capillary tubing into the 5 mm hard glass tubes sealed into R. As a further safeguard to diffusion backward as well as distribute the nitrogen entering the chamber, a plug of glass wool was placed at the inner end of the entrance capillary.

The nitrogen supply was contained in a large carboy connected at A (Fig. 4). The gas first passed through the drying tower D, containing calcium chloride and soda lime,

then through E and G. Tube E contained copper, copper oxide, soda lime, and calcium chloride in the order named to remove traces of oxygen and oxidize traces of organic matter. The copper and oxide were heated with a gas burner. Connection between D and E was a ground glass joint made tight with a little marine glue. Tube G contained copper and oxide heated to redness by means of a platinum foil electric heater. Nitrogen was drawn through the apparatus by drawing a measured volume of liquid from the aspirator O.

The mercury was condensed in H and the oxygen caught at L. It was first attempted to catch the oxygen on a roll of copper gauze suspended in the tube and heated to redness by an electric heater, but we found that the oxide had a tendency to scale off of the copper. This trouble was eliminated by hanging a platinum cup beneath the gauze to catch the scales. Then it was found that all of the oxygen was not fixed on the copper so a coil of fine iron wire loosely wound on a porcelain rod was hung above the copper.*

The remaining details are taken up in the method of operation as follows: Cocks B, F, and M, Fig. 4, were closed and the apparatus exhausted through C. Then C was closed and nitrogen admitted through B. E and G were heated up and a current of nitrogen forced through the apparatus and out at N until all traces of oxygen were thought to have been driven out. Then the tip of tube J was cut off, M closed, and the gases passed out at J while the temperature was being brought up in R. The current for the large furnace was taken from storage cells. By using 50 cells in two sets of 25 each, and these sets connected in parallel, we were able to keep the temperature constant within 1° for several hours, after it had once been established. A small sliding resistance and an accurate ammeter were indispensable aids. The thermo-

* A quantity of iron wire sufficient to take care of all the oxygen in some of our runs would have been too large for the tube, hence the combination of copper and iron. That no appreciable amount of oxygen was left in the nitrogen entering R after passage over the two copper gauzes in E and G is shown by the good agreement between oxygen and mercury in our results.

element wires enclosed in a porcelain tube in the position shown in Fig. 5 were so arranged that the temperature at any place along R could be taken. The small electric heater I kept the gases hot until they reached H. It could be pushed completely back into the larger furnace.

In the tube at K was placed an electric glower, made of platinum wire wound on a porcelain tube over which slipped a quartz tube wrapped on the outside with fine iron wire. When the quartz was heated to redness by passing a current through the platinum wire, the iron was made sufficiently hot to take up any oxygen diffusing beyond H while equilibrium was being established in R.[29] It required at least 2 hours to establish the temperature constant and the gases were passed out at J for some time after this in order to ensure equilibrium conditions before the run was started. The rate of flow of nitrogen during this time was the same as that used after the run was begun. The mercury condensed in H was now driven out with a small flame, J sealed off, M opened to O, the current in the glower at K shut off, and the small bore cock F, whose tip just touched a water surface, opened. Aspiration was started by drawing liquid from O and admission of nitrogen at A regulated so that an occasional bubble escaped at F, which ensured that the whole apparatus was always at atmospheric pressure. At the end of the experiment, M was closed, the heater at I pushed back into the large furnace and the small tube S (Fig. 5) sealed off quickly. The mercury was collected from H with the aid of a little weak nitric acid, washed, and dried in a vacuum desiccator. The increase in weight of the copper gauze and iron coil gave the oxygen.

The nitrogen used in these experiments was made by removing oxygen from air with a burning jet of hydrogen according to the method of Hulett.[30] With a long combustion furnace we were able to make 45 liters in less than 2 hours.

Results.—The results have been calculated to partial pressure of oxygen from the *oxygen equivalent* of the weight

of the mercury, since a small error in the weight of the oxygen makes a considerable difference in the calculated pressure, and experience has shown that the oxygen weight is less reliable. The scheme of calculation follows:

$$\text{Vol. } N_2 = \text{cc drawn from aspirator} \times \frac{\text{temp. of dissociation}}{\text{temp. in aspirator}}$$

$$\text{Vol. } O_2 = \text{wt. Hg} \times 0.08 \times \frac{22412}{32} \times \frac{760}{\text{barometer}} \times \frac{\text{temp. dissociation}}{273}$$

$$\text{Partial pressure oxygen} = \frac{\text{Vol. } O_2}{\text{Vol. } N_2 + 3 \times \text{Vol. } O_2} \times \text{barometer.}$$

The temperatures are of course on the absolute scale.

Varying the rate of flow of the nitrogen until slower rates show no increase in the calculated pressure ought to tell us whether equilibrium is being reached or not. The results of a series of experiments at 410° C in order to determine the rate necessary for equilibrium are given in Table III. The reaction chamber in this case was 18 cm long and contained 150 grams oxide and 30 grams ferric oxide as catalyst, which almost completely filled it. In judging whether equilibrium has been reached it must be remembered that the quantity of oxide is diminishing from run to run. The problem was further complicated by the fact that the lower limit of a slow rate was soon reached when diffusion backward from R began. This distinctly happened in run No. 13. The volume of nitrogen in these runs was determined by weighing the water drawn from the aspirator and converting to cubic centimeters. Correction of this volume for aqueous tension was applied. The result of these experiments did not tell us whether equilibrium was reached or not, but slight changes in pressure for great changes in rate showed that we were near it.

Table IV gives results with a larger (25 cm) reaction chamber and a fresh charge.

Table V gives results at 375° C with the larger chamber and an initial charge of 150 grams oxide. The volume of nitrogen in these two series was measured by drawing mercury into accurately calibrated flasks.

TABLE III—DYNAMIC METHOD

Run No.	Time Hours	Volume nitrogen			Vol. N_2 410°	Rate cc per minute	Wt. O_2	Mercury wt. = O_2		Partial pressure oxygen mm
		cc	°C	Bar						
7	$2^1/_4$	1000	28	751.4	2184	16.2	0.1934	2.539	0.2031	82.7
8	$3^3/_4$	1000	28.5	762.5	2175	9.7	0.2349	2.946	0.2357	92.0
9	$3^1/_2$	555	28	760.0	1213	5.8	0.1420	1.795	0.1426	97.1
10	$2^1/_2$	351	30	758.0	758	5.0	0.0897	1.1263	0.0901	97.2
11	$2^1/_2$	465	30.5	754.8	1004	7.4	0.1137	1.4294	0.1143	94.6
12	$2^1/_2$	228	28.5	750.6	496	3.3	0.0618	0.7670	0.0614	99.4
13	5	201	27.5	757.4	440	1.5	0.0564	0.7245	0.0580	103.7

TABLE IV

20	$3^1/_4$	350	28	761.0	794	4.1	0.1036	1.303	0.1042	103.4
21	$1^1/_4$	191	27	757.2	435	5.8	0.0586	—	—	104.8
22	$1^2/_3$	250	28	758.4	567	5.7	—	0.8992	0.0719	101.2

TABLE V—375° C

					375°					
—	—	—	—	—	—	—	—	—	—	—
15	3	250	28	760.5	538	2.9	—	0.2322	0.0186	37.1
16	5	500	28	762.8	1076	3.6	0.0431	0.4965	0.0397	39.4
17	$3^1/_2$	500	27	753.3	1080	5.1	0.0415	0.4995	0.0399	39.3
18	$2^2/_3$	500	26	764.8	1083	6.8	0.0366	0.4660	0.0373	37.2
19	$4^3/_4$	500	25.5	764.6	1086	3.8	0.0352	0.4910	0.0393	38.7

Calculated for 410° 101 mm, for 375° 40 mm.

Calculation of results by this method involves two assumptions, first, that the partial pressure of the oxygen in nitrogen purified by passage over copper-copper oxide is negligible and, second, that both oxygen and mercury vapor follow the gas laws. Both assumptions are justified within the errors of experiment. It has been difficult to get as accurate results with this apparatus as the dynamic method might be expected to give, mainly on account of the very slow rate at which the nitrogen must be passed in order to ensure saturation.

The Dissociation of Mercuric Oxide

Discussion of Results.—We find that on a large scale plot of all our results of partial pressure of oxygen against tem-

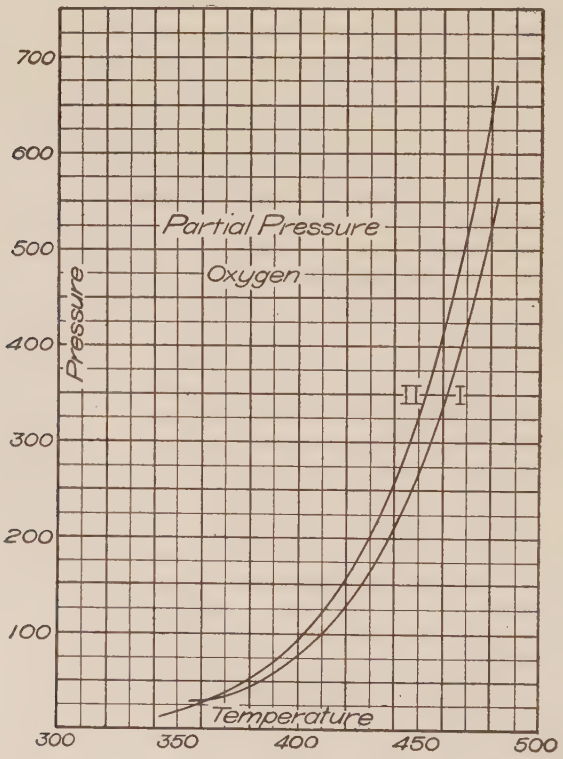

Fig. 6

perature, a smooth curve may be drawn through the points indicated by the static method. Points by the dynamic method and of the higher temperatures by the submerged bulb method lie very closely on this curve, while those of the lower temperatures of the latter lie irregularly below it. The dynamic method confirms the values obtained by the static one as was to be expected, since, as already pointed out, the results by the submerged bulb at lower temperatures were less to be relied upon. The final curve is shown in Fig. 6, and from it we have constructed the following table:

° C	Total pressure mm	Partial pressure oxygen mm
360	90	30
370	108	36
380	141	47
390	180	60
400	231	77
410	303	101
420	387	129
430	498	166
440	642	214
450	810	270
460	1017	339
470	1275	425
480	1581	527

Curve II, Fig. 6, shows extrapolated values from Pélabon's formula.

Heat of Dissociation.—Having the dissociation pressures at two different temperatures allows us to calculate the heat of dissociation from the equation of van't Hoff, called by Nernst the *equation of the reaction isochore*,

$$\frac{d \ln K}{dT} = - \frac{U}{RT^2} \qquad (1)$$

In the integration of the equation U is generally regarded as constant but a more accurate value may be calculated by regarding it as a linear function of the temperature,

$$U = U_o - CT \qquad (2)$$

and calculating according to the integrated form given by Lewis[31] in his work on silver oxide,

$$\ln \frac{P_1}{P_2} = -\frac{U_o}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) + \frac{V}{R}\left(\frac{P_1}{T_1} - \frac{P_2}{T_2}\right) + \frac{R - C}{R} \ln \frac{T_1}{T_2} \quad (3)$$

where C is the diminution in the heat capacity of the system during the decomposition and V the total change of volume of the *solid* phase. For mercuric oxide the term containing V is negligible and may be dropped out. The last term in (3) is a correction term and an approximate value for C will do. C is the diminution in heat capacity of 2 grams molecules of mercuric oxide after complete dissociation. The specific heat of the solid oxide given in Landolt-Börnstein's tables as due to Regnault is 0.0518, the molecular heat is therefore 11.2 and for two mols 22.4. The molecular heat of mercury vapor at constant volume following the rule of monatomic gases may be taken as 3, and that of oxygen 5. Then for two mols of mercury vapor and one of oxygen the result is 11.0, whence C = 11.4. Since the dissociation results in three mols, 3R must be substituted wherever R occurs in the equation.

In applying equation (3) to our results, we have selected the following data and used them in pairs:

(*a*)	400° C	231 mm
(*b*)	450°	810
(*c*)	480°	1581

for U_o (*a*) and (*c*) give 76430 cal., (*b*) and (*c*) 76320, and (*a*) and (*b*) 76490 cal. We may take as the value of U_o the average, 76400 cal.

The heat of formation of mercuric oxide according to equation

$$Hg_{liquid} + O_{gas} = HgO_{solid}$$

has been determined by J. Thomsen[32] to be 22000 cal., by Nernst[33] 20700 cal., and more recently by Varet[34] 21500, all by indirect methods. In order to compare our value of U, the heat of vaporization of mercury must be subtracted. Kurbatoff[35] found the molecular heat of vaporization at the

boiling point (358° C) to be 13500 cal. U at 358° calculated from equation (2) is 69200, from half of which subtract 13500 giving 21100 cal. as heat of reaction between liquid mercury and oxygen gas at 358° C exclusive of external work. In order to rigidly compare with results obtained calorimetrically, this value must be calculated to room temperature by aid of equation expressing change of heat of reaction with temperature,

$$\frac{U_2 - U_1}{t_2 - t_1} = C - C' \qquad (4)$$

where $U_2 = 21100$ is heat developed at 358° (t_2), and U_1 at 18° (t_1); $c' = 11.2$ cal. heat capacity of the solid oxide and $c = 10.1$ cal., heat capacity of the reacting oxygen at constant pressure plus the liquid mercury; whence $U_1 = 21500$ cal. The average of the calorimetric values is 21700 from which must be subtracted the external work $^1/_2$ RT cal. giving 21400 cal. The agreement is excellent.

Calculation of the Equation of the Curve of the Dissociation Pressure

This may be done directly with the aid of the Nernst formula[36]

$$\log P = -\frac{\lambda_o}{4.571\,T} + 1.75 \log T - \frac{\varepsilon}{4.571} T + C \qquad (5)$$

in which the constants λ_o, ε, and C may be found by taking the values of P at three different temperatures. From the data (*a*), (*b*), and (*c*) given above, we get

$$\lambda_o = 24105 \quad \varepsilon = 0.004723 \quad C = 5.9461 \qquad (6)$$

whence the equation of the curve becomes

$$\log P = -\frac{5273.5}{T} + 1.75 \log T - 0.001033\,T + 5.9461 \qquad (7)$$

We are now in a position to calculate the dissociation pressure of mercuric oxide at any temperature either from equation (3) or equation (7). Taking as our data in (3), $U_o = 76400$ and a pressure of 810 mm at 450° C, we obtain

as the pressure at 500° C 2395 mm. Substitution in (7) gives the same value, corresponding to a partial pressure oxygen 798 mm, while Pélabon's observed value is somewhat higher, 985 mm.

At lower temperatures, taking again as our data U_o = 76400 and a pressure of 231 mm at 400° C in (3), we obtain practically identical values from (3) and (7), at 200° C 0.10 mm, at 25° C 1.9×10^{-8} mm. Extrapolated values from Pélabon's formula give for 200° 0.04 mm and for 25° 3×10^{-12}, values smaller than the above, just as might be expected from the intersection of the curves as shown in Fig. 6.

It has been shown in distilling amalgams under reduced pressure with a slow current of air drawn through,[19] that the base metals are oxidized in the vapor phase. That mercury does not oxidize under these conditions (*i. e.*, 5 mm partial pressure oxygen and 200° C) is probably due to slow rate of reaction, as the partial pressures of mercury and oxygen in the still are much greater than are necessary to fulfil the equilibrium pressures as indicated by our calculation at 200°.

The extraordinarily low values of the dissociation pressure at room temperatures indicates that in the presence of mercury the oxide is perfectly stable in air. At the same time if no mercury is present, no pressure of oxygen, however great, could prevent theoretically some decomposition of the oxide, since there would be a vacuum to mercury vapor. Mercury then can oxidize under atmospheric conditions and it is merely a question of rate. If the explicit cause of the dirtying of mercury is to be found in the oxidation of the metal itself the role of the suboxide should be considered.

Platinum as Catalyst.—Finely divided platinum acts as a catalyzer for the dissociation of mercuric oxide but we have been unable to get concordant quantitative results with it. The pressures experimentally obtained by its use in either the static or submerged bulb methods were always too high, while the inherent experimental errors, aside from incomplete

expulsion of air, were due to the slow evolution of the gases and were in the opposite direction. There can hardly be any question but that platinum dissolves both of the dissociation products to some extent. It was hoped that the platinum would soon become saturated and then we should obtain correct values but this was apparently impossible.

Now it can be shown that if either of the products of dissociation is in excess, then the *total pressure* will be increased, for if mercuric oxide decomposes according to the following equation,

$$2HgO \rightleftarrows 2Hg + O_2$$

then the mass law requires that

$$\frac{C^2_{Hg} \times C_{O_2}}{C_{HgO}} = \text{constant}$$

where C represents concentration. Assuming the densities of the gases to be normal we may substitute their partial pressures for concentrations. Let p be the partial pressure of oxygen and m that of mercury, then since the pressure of the solid is a constant

$$pm^2 = K \tag{8}$$

where K is the dissociation constant. Let P be the total pressure, then $P = p + m$ and

$$P = \frac{K}{m^2} + m \tag{9}$$

$$\frac{dP}{dm} = -\frac{2K}{m^3} + 1$$

The theorem of maxima and minima requires, in order for P to have a minimum value, $\frac{dP}{dm} = 0$.

$$-\frac{2K}{m^3} + 1 = 0 \tag{10}$$

$$m^3 = 2K = 2pm^2 \tag{11}$$

$$m = 2p \tag{12}$$

Equation (12) is satisfied only when the mercury vapor and oxygen are in equivalent proportions. This proof can

be made perfectly general, and thus we arrive at the interesting conclusion that the smallest possible *total* pressure of any number of gases uniting to form one definite solid and in equilibrium with that solid, occurs when the gases are in the same proportions in which they exist in the solid phase. The results of Isambert[37] with ammonium carbamate accord with this conclusion.

The Identity of the Red and Yellow Oxides.—There has been some controversy in the literature over the identity of the red and yellow oxides. Measurements of electromotive force in various types of cells[38] have led Cohen[39] to the conclusion that they are modifications and not identical, having apparently different contents of energy. But Ostwald[40] contends that the small electromotive force observed is due to the different rates of solubility of the forms owing to the much finer state of division of the yellow.[40'] This view is borne out by Varet's[41] determination of their identical heats of formation. Additional confirmation is found in the only slightly different solubilities of the two forms in the alkali-halide solutions,[42] in oxalic acid,[43] and in pure water.[44]

More recently Schoch[45] has concluded that the red and yellow are not identical, based mainly on qualitative distinctions of color and crystalline form and a difference in their dissociation pressure. He employed a static instrument consisting essentially of a bulb containing the oxide to which was attached a capillary tube ending in an open manometer. The apparatus was arranged so that it could be exhausted and the construction was such that the condensation of mercury was minimized. The results are discordant and much higher than our values for both the red and the yellow. It is stated that ground red oxide exerts a greater tension than coarse oxide and that the yellow oxide gives a pressure of near an atmosphere at 310° while the finely ground red gives only half as much. It is also stated that "the yellow oxide shows its own proper tension only for a short time when first heated." This statement seems to be based upon the fact that a sample showed on first heating a pressure of 660 mm. It was then

allowed to cool, the apparatus reexhausted, and when heated up again to about the same temperature showed a pressure of only 200 mm. The conclusion drawn is that the initial heating converted it into the red variety since its pressure fell towards that assumed for the red. Is it not more probable that the samples used by Schoch contained enough impurity, possibly in the shape of occluded gases, to account for the high values obtained? The lower pressure obtained for the yellow on reheating may have been due to the removal of some of the gaseous impurity by the exhaustion of the apparatus between experiments, and seems to us to be a more probable explanation of the facts than transition into the red form. We have heated the yellow oxide for several hours at 475° without noting any change in color, after cooling. Its rate of decomposition without a catalyst is not noticeably different from the red.

We have made a series of measurements of the dissociation pressure of the yellow oxide by our static method with ferric oxide as catalyst. This static method permits the removal of volatile impurities which is an important point in view of the possible serious errors of most static instruments. The resulting curve coincides with the red and confirms Ostwald's identity theory. The data upon which this conclusion is based follows:

KAHLBAUM'S YELLOW OXIDE AND Fe_2O_3

° C	Total pressure mm	Partial pressure oxygen	
		(Observed)	(Calc.)
477.1	1474	491.3	494
448.0	780	260	258
415.0	342	114	113

Summary

1. It has been shown that the decomposition of mercuric oxide is catalyzed by platinum and certain metallic oxides.

2. The dissociation pressure of mercuric oxide has been measured from 360° C to 480° C.

3. Pressures calculated to 200° C and room temperature have shown that the oxide is stable in the presence of mercury in the air, even under greatly reduced partial pressure of oxygen.

4. Mercury may oxidize under atmospheric conditions, it is a question of rate, and the rate is evidently markedly affected by catalyzers.

5. The heat of formation as calculated from the dissociation pressure has been found to agree with the calorimetric results.

6. The dissociation pressure of the yellow oxide has been shown to be the same as that of the red oxide, confirming the identity theory.

7. It has been shown that the mass law requires that a solid which dissociates completely into gases is in equilibrium with those gases at a minimum total pressure when none of the gaseous components are in excess.

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